The influence of polymer on the diffusion of a spherical tracer

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We analyze how the addition of a small number of polymer molecules influences the diffusion constant of a spherical tracer, whose radius is small compared to the size of the polymer. We show that the polymer chain can be regarded as a two-dimensional object which is an impenetrable obstacle for the tracer. It is also shown that the diffusion constant of the tracer, in contrast to the solution viscosity, is independent of chain length, depending only on the monomer concentration. © *1999 American Institute of Physics.* [S0021-9606(99)52437-9]

The analysis in this note was stimulated by experimental studies of the influence of the addition of polymer molecules on the conductance of ionic channels.[1] To analyze this influence it is desirable to first gain a clear understanding of how the addition of polymers changes ionic conductivity of bulk solutions. To gain insight into this problem in this note we ask a simpler question: how does the presence of long polymer molecules influence the motion of an uncharged spherical tracer diffusing in the solution?

Many important cellular functions are controlled by the transport of ions through lipid bilayer membranes surrounding cells.[2] Ions in aqueous solution cannot cross poorly polarizable membranes;[3] instead they pass through hydrophilic pores of ion channels formed by membrane-spanning proteins.[4,2] One of the most challenging topics in modern molecular biology is that of determining the structure and transport properties of hydrophilic pores as well as the mechanisms responsible for conformational transitions between states of different ionic conductance. The use of water-soluble polymers to study ion channels has recently been suggested as a useful tool to estimate structural parameters relevant to the properties of channels.[5,1]

Experimental evidence shows that while the solution viscosity depends on the chain length, the conductance depends only on the concentration of monomers.[1] An example of this behavior given in Fig. 1 demonstrates a significant increase of solution viscosity due to the increase of chain length, unaccompanied by a significant decrease in conductance.

To understand this seeming contradiction to traditional ideas, according to which the conductivity is inversely proportional to the viscosity, we consider a simplified problem in which a neutral spherical tracer diffuses in a solution containing long polymer molecules. We will see that the polymer chain can be regarded as a two-dimensional object, impenetrable to the tracer. It will be shown that the diffusion constant of the tracer behaves qualitatively like the conductivity. In contrast to the solution viscosity, it is independent of chain length, and depends only on monomer concentration.

In studying the influence of added polymer on the diffusion constant of the tracer, we assume that the polymer molecule is modeled as a Gaussian chain comprised of $N(\gg 1)$ monomers (beads) connected by bonds, each of which is of length a. Further, we model the tracer as a spherical ball of radius b, assumed to be much larger than a and much smaller than the characteristic size of the polymer molecule which is the radius $R_N \propto a N^{1/2}$. We thus have $a \ll b \ll a N^{1/2}$.

A most naive picture represents the polymer chain by a set of N monomers which uniformly fill a sphere of radius R_N. From this picture one might conclude that the larger the size of the polymer chain, the easier it will be for the tracer to pass through the domain occupied by the chain. Indeed, since the volume of the sphere, v_N, is proportional to $N^{3/2}$, the concentration of monomers in the sphere is proportional to $N/v_N \propto N^{-1/2}$, so that increasing N makes it easier for the tracer to pass through the domain occupied by the chain. We will show that, in fact, the tracer cannot pass through a long chain without perturbing it since the chain covers a two-dimensional surface which blocks tracer motion.

The pitfall in the preceding argument is that a picture of the polymer as a collection of N monomers uniformly filling a sphere of radius R_N appears only after averaging over all chain configurations. This was first pointed out by Kuhn.[6] Later this question was investigated in greater detail by Solč and Stockmayer[7] and later by Rudnick and Gaspari.[8] Related studies were carried out by Rubin and Mazur.[9]
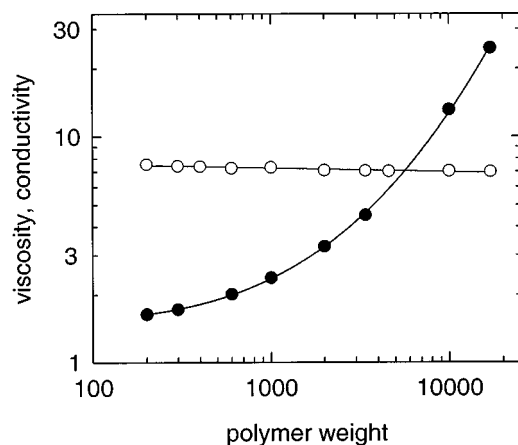
FIG. 1. The viscosity (in centistokes, ●), and conductivity in (mS/cm×10, ○) of 15 weight percent PEG solutions in 0.01 M (aqueous) KCl at room temperature as a function of the molecular weight of the polymer.

To support our assertion that the domain occupied by a polymer tends to block passage by the tracer, consider a particular chain configuration. This can be visualized as a curve, $\{\mathbf{R}(s')\}$, where s' is a parameter which takes values between 0 and s. For a Gaussian chain this curve can be considered as a Wiener trajectory $\{\mathbf{R}(s')\}$ where s' is a "time" which varies between 0 and s. The parameter s is related to the bond length a and the number of monomers by

$$6Ds = Na^2, \tag{1}$$

where D is an effective diffusion constant[10,11] that determines the probability that the trajectory representing the polymer configuration is realized.

We next have to explain what we mean by the term impenetrability. Let $\{\mathbf{r}(t')\}$ be a trajectory of the center of the tracer diffusing in the space free of chains for a time t, where $0 \leq t' \leq t$. Recalling that b is the tracer radius we will say that the tracer passes through the polymer provided that $|\mathbf{r}(t') - \mathbf{R}(s')| > b$ throughout the range of possible values of t' and s'. When this condition does not hold we will say that the tracer that moves along the trajectory $\{\mathbf{r}(t')\}$ does not penetrate the polymer.

In this picture a tube of radius b centered on the curve $\{\mathbf{R}(s')\}$ forms a domain forbidden to the center of the spherical tracer (Fig. 2). If different parts of this tube overlap, the domain occupied by the chain is impenetrable to the tracer [Fig. 2 (top panel)]. When such overlapping is negligible [Fig. 2 (bottom panel)], the tracer can traverse the domain. In that case the tube volume, $V_b(\{\mathbf{R}(s')\})$, will be proportional to b^2. If this dependence is absent, the degree of overlap is significant which effectively blocks the passage. One can estimate the degree of overlap by analyzing the dependence of tube volume, $V_b(\{\mathbf{R}(s')\})$, on the tracer radius b. Hence we are led to consider properties of the volume swept out by a fictitious spherical particle of radius b, the center of which moves along the trajectory corresponding to the polymer configuration, $\{\mathbf{R}(s')\}$.

Thus, to decide whether the tracer passes through the polymer one has to evaluate the dependence of the volume $V_b(\{\mathbf{R}(s')\})$ on the radius of the tracer, b. While this depen-
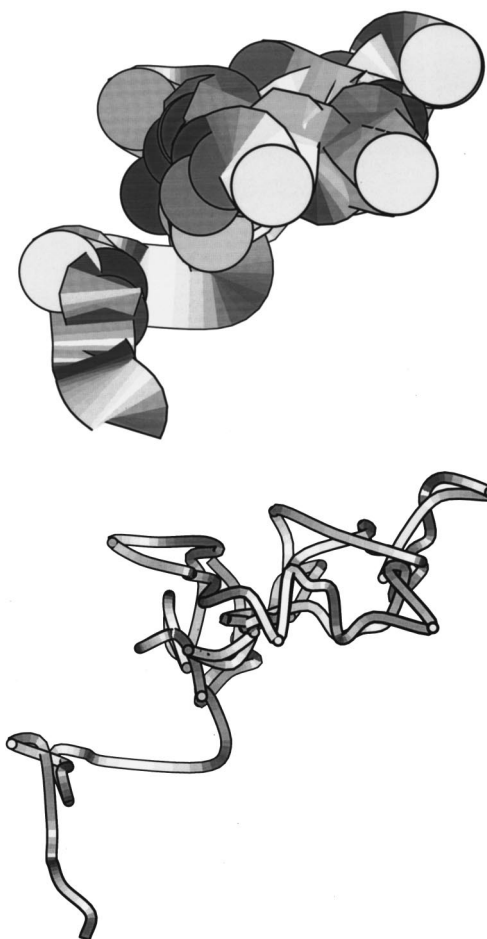

FIG. 2. A tube of radius b centered on the curve generated by a Gaussian random walk with $N=100$ steps each having a mean square length equal to 1, i.e., $a=1$, $b=1$ in the top panel and $b=0.1$ in the bottom panel. The radius of gyration of this realization of the polymer molecule represented by the random walk is $R_g = 3.15$ which is equal to the most probable value of R_g for $N=100$. The figures were produced using the Molscript program (Ref. 15).

dence on b cannot be estimated in the case of a specific configuration, the average of this quantity over all configurations has been found in Ref. 12 to be

$$\langle V_b(\{\mathbf{R}(s')\})\rangle = \frac{4}{3}\pi b^3 + 8b^2\sqrt{\pi Ds} + 4\pi Dbs$$

$$= \frac{4}{3}\pi b^3 + 4\sqrt{\frac{2\pi}{3}}\,ab^2\sqrt{N} + \frac{3}{2}\,\pi a^2 bN. \tag{2}$$

This formula is derived in the appendix, to make the paper self-contained.

When $N \gg (b/a)^2$ the average volume calculated from Eq. (2) is approximately given by

$$\langle V_b(\{\mathbf{R}(s')\})\rangle \approx \frac{2}{3}\pi a^2 bN. \tag{3}$$

While this has been derived for the volume averaged over all possible realizations, we assume that it holds for the overwhelming majority of realizations as well. Since the averaged volume is proportional to b it may be interpreted as the volume of a pancake object with a thickness proportional to

b and the area proportional to Na^2 [Fig. 2 (top panel)]. This is the origin of our earlier statement that the chain densely covers a two-dimensional surface.

The major point is that the average volume is proportional to the first power of b rather than to its square. This means that different parts of the tube overlap. As a consequence the chain is an impenetrable obstacle to passage by the tracer. This may be considered as a consequence of the fact that a Gaussian chain is a curve with a fractal dimension of 2, which means that it densely covers a two-dimensional manifold.[13] Thus, a picture emerged from our considerations, of a tracer diffusing among impenetrable domains occupied by polymers differs dramatically from one based on the naive picture described earlier.

Both pictures will be used to gauge the degree to which the polymer impedes the diffusive motion of the tracer. This allows us to see the resemblance and distinction between results predicted by the two models. We will assume that the density of obstacles is sufficiently small so that the tracer motion is still diffusive. The presence of obstacles is taken into account by replacing the obstacle-free diffusion constant of the tracer, D_0, by an effective diffusion constant D_{eff}. When the volume fraction, ψ, of obstacles is small, $\psi \ll 1$, the relation between these two constants is expressed as

$$D_{\text{eff}} \approx D_0(1 - \alpha \psi), \qquad (4)$$

where α is a constant which depends on the shape of the obstacles.

In the naive picture which assumes that each monomer is an independent scatterer, the dependence of ψ on the radius b satisfies $\psi \propto b^3 c_m$, where c_m is the concentration of monomers. When the polymer is treated as a Gaussian chain this dependence changes to $\psi \propto a^2 b c_m$. This follows from Eq. (3) by multiplying the averaged volume by the concentration of scatterers, c_m/N. By the same line of argument we find that for a linear chain $\psi \propto a b^2 c_m$. The striking conclusion to these considerations is that ψ, and hence D_{eff} depends on c_m and is independent of chain length, regardless of which model of the chain is used.

The fact that D_{eff} is independent of chain length might seem to be surprising since the viscosity of the solution increases sharply with chain length.[10] However, viscosity of the polymer solution is determined by the energy dissipation on length scales much larger than those associated with the dissipation due to the tracer's motion. This heuristic argument suggests why D_{eff} should be insensitive to both chain length and solution viscosity and close to D_0 as well. This behavior is qualitatively similar to that of the conductivity shown in Fig. 1. However, there is an obvious gap between the mobility of ions, and therefore the conductivity, and the diffusion of the neutral spherical tracer analyzed in the present report.

An aspect to be emphasized is that we have discussed an intermediate regime in which the tracer radius is large compared to the bond (Kuhn) length but small compared to the size of the chain. When the size of the tracer is small compared to the bond length, we also expect that the diffusion constant should be nearly unchanged as compared to its value in pure solvent, D_0. Presumably the naive picture suffices to treat this case. At the same time, when the size of the tracer is comparable with the chain size the diffusion coefficient is inversely proportional to the solution viscosity.

In summary, our analysis of the influence of polymer molecules on the diffusive properties of a spherical tracer has shown that the diffusion constant for the tracer is close to that in pure solvent in spite of significant growth of solution viscosity. To lowest order the correction to the diffusion constant is proportional to the first power of monomer concentration and is independent of chain length. Different models of the chain lead to different dependences of the effect on the radius of the tracer. The present results have been derived using four major assumptions: (1) The tracer radius is much larger than the bond length and much smaller than the size of the polymer molecule. (2) The polymer molecules can be approximated as Gaussian chains. (3) Chain dynamics can be neglected. (4) The volume fraction of the polymer is small. In addition, we assume that the diffusion constant of the tracer is independent of its distance from the polymer.

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APPENDIX: DERIVATION OF EQ. (2)

The volume $V_b(\{\mathbf{R}(s')\})$ is defined by integral over an indicator function

$$I_b[\mathbf{r}, \{\mathbf{R}(s')\}] = \begin{cases} 1, & \min_{0 \leq s' \leq s} |\mathbf{r} - \mathbf{R}(s')| < b \\ 0, & \text{otherwise} \end{cases} \qquad (A1)$$

which is to say,

$$V_b(\{\mathbf{R}(s')\}) = \int I_b[\mathbf{r}, \{\mathbf{R}(s')\}] d\mathbf{r}. \qquad (A2)$$

Thus, to find the average of $V_b(\{\mathbf{R}(s')\})$ with respect to all Wiener trajectories starting from $\mathbf{R}(0)$, it is necessary to find the average of $I_b[\mathbf{r}, \{\mathbf{R}(s')\}]$. But this average is equal to the fraction of Wiener trajectories which have visited a spherical domain of radius b centered at $\mathbf{r}$ at least once during the time s. The fraction indicated is equal to the probability that a diffusing particle, initially at $\mathbf{R}(0)$, has been trapped during a time interval equal to s on the surface of an absorbing sphere of radius b centered at $\mathbf{r}$. This probability is known to be[14]

$$\langle I_b[\mathbf{r}, \{\mathbf{R}(s')\}] \rangle = \frac{b}{|\mathbf{r} - \mathbf{R}(0)|} \text{erfc} \left\{ \frac{|\mathbf{r} - \mathbf{R}(0)| - b}{\sqrt{4Ds}} \right\} \qquad (A3)$$

for $|\mathbf{r} - \mathbf{R}(0)| > b$. An integral over $\mathbf{r}$ of this function leads to the result in Eq. (2).

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